PREPARATION AND CHARACTERIZATION OF SBA-15 SUPPORTED Co/Zn CATALYST FOR FISHER TROPSCH SYNTHESIS: EFFECT OF COBALT LOADING

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ABSTRACT

The influence of promoter (Zn) and effect of cobalt loading on the physiochemical and catalytic properties of mesaporous silica Co/SBA-15 catalysts for the Fischer-Tropsch (FT) synthesis was investigated. SBA-15 was synthesized as support. The mesoporous silica Co-Zn/SBA-15 catalysts were prepared by incipient wetness impregnation method. Cobalt nitrate and zinc nitrate were used as sources of metal that introduced onto support with same zinc loading (20 wt %) and different cobalt loading (5 wt %, 10 wt%, 15 wt %). The characterization of catalysts was performed by using Fourier transform Infrared (FTIR) and Scanning Electron Microscopy (SEM). The results for FTIR were identification of Si-O-Zn and Si-O-Co functional group because of the present of zinc or cobalt onto silica SBA-15 support. Besides that, the identification of metal inside SBA-15 was determined by comparing the pure SBA-15 with the incorporated metal on SBA-15. For SEM analysis, the image shows that the rope like domain aggregated to wheat like microstructure. Incorporation of Co and Zn did not change the morphology of the support. For this research, the characterization of the catalyst by selecting Zn as promoter have quiet similar characterization with noble metal that already investigate.

ABSTRAK

Pengaruh zink sebagai penyumbang dan pengaruh kehadiran kobalt pada sifat-sifat fizikal dan kimia dan sifat katalitik dari mangkin silika Co/SBA-15 berliang meso untuk Fischer-Tropsch (FT) sintesis telah diteliti. SBA-15 disintesis sebagai penyokong/pendukung. Pemangkin silika berliang meso Co-Zn/SBA-15 disediakan dengan kaedah impregnasi yang sedikit basah. Cobalt nitrat dan zink nitrat digunakan sebagai sumber logam untuk menghasilkan pemangkin. Kuantiti zink yang dimasukkan adalah sama (20 wt%) dan kuantiti kobalt yang berbeza (5 wt%, 10% wt, 15% wt). Sifat-sifat mangkin di percirikan dengan menggunakan transformasi Fourier Infrared (FTIR) dan Mikroskop Elektron (SEM). Keputusan untuk FTIR adalah pengenalan Si-O-Zn dan Si-O-Co kumpulan berfungsi kerana zink atau kobalt hadir di atas SBA-15. Selain itu, pengenalan logam di dalam SBA-15 juga ditentukan dengan membandingkan SBA-15 dengan SBA-15 yang diimpregnasikan dengan unsur logam. Untuk analisis SEM, gambarajah menunjukkan sifat SBA-15 dan SBA-15 yang telah dimpregnasikan dengan logam bersifat seperti lingkaran tali yang berpintal dan pengaruh Zn dan Co tidak sama sekali mengubah bentuk morfologi penyokong . Untuk kajian ini, didapati ciri-ciri mangkin dengan pemilihan Zn sebagai unsur penggalak mempunyai ciri-ciri yang sama dengan logam aktif yang telah digunakan sebelum ini .

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.

FTIR	Fourier Transform infrared Spectra
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy
FT	Fisher Tropsch
WGS	Water Gas Shift
TEM	Transmission Electron Microscopy
SCR	Selective Catalytic Reduction
Zn	Zinc
Co	Cobalt
Al_2O_3	Alumina
CoO	Cobalt Oxide
TEOS	Tetraethylorthosilicate
MSI	Metal Surface Interaction
XRD	X-Ray Diffraction
GTL	Gas to liquid

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CHAPTER 1

INTRODUCTION

1.1 Background of the study

1.1.1 Fisher-Tropsch Process

In 1902, Paul Sabatier and Jean Sanderens discovered a way of converting Carbon Monoxide (CO) and Hydrogen (H_2) to Methanol (CH_3OH) (Hill,1982). Franz Fischer and Hans Tropsch developed this synthesis to mainly oxygenated products and hydrocarbons in 1923 using alkalized iron as a catalyst (Davis, 1997). In 1925 the two German scientists further developed this reaction by converting the mixture of (CO) and (H_2) which is called Synthesis Gas or "Syngas" in a laboratory to oxygenated products and liquid hydrocarbons using cobalt and nickel catalysts at atmospheric pressures.

Figure 1.1: Developers of the Fischer -Tropsch Synthesis Process (Shalchi, 2006)

In order to commercialize the FT reaction to became FT process, the production of raw hydrocarbons can be refined and upgraded into different fuels like gasoline, diesel, and other products. In the mid 1930s, a number of Fischer-Tropsch plants were constructed, and by 1938, over 590,000 tons of oil and gasoline were being produced annually in Germany from synthesis gas manufactured from coal.

During 1930s, plants were also constructed in Japan, Britain, and France. During World War II Germany operated nine F-T plants that produced 12,000 barrel/day of fuel. Those plants that were not destroyed during the war were shut down subsequently as cheap petroleum crude and natural gas became available. One country which has continued to pursue the development of indirect coal liquefaction by Fischer-Tropsch process is South Africa.

In the following years many companies like Mobile, Sasol, Shell, Rentech, ConocoPillips, Syntroleum, and BP, have started technology developments of the Fischer-Tropsch process either in response to oil crises, or due to high crude oil price. The main purpose of these developments is to make any industrial plant use this technology to become commercially successful.

Fischer-Tropsch Synthesis (F-T) converts synthesis gas (CO and H_2) which can be made from coal, natural gas, petroleum residues, biomass, and any carbonaceous materials to long chain hydrocarbons. If liquid petroleum-like fuel, lubricant, or wax is required, then the Fischer- Tropsch process is the right process that can be applied. This is an alternative route to obtain fuels and chemicals rather than the current dominant petroleum resources. Fischer-Tropsch synthesis now is becoming competitive to petroleum due to its improved catalysts and processes (Shalchi, 2006).

Currently, Gas to Liquids (GTL) is the major focus on the (F-T). Chemically the (GTL) in Fischer-Tropsch process is a series of catalyzed chemical reactions in which carbon monoxide and hydrogen are converted into liquid hydrocarbons of various

forms. The principal purpose of this process as mentioned above is to produce a synthetic petroleum substitute. The original basic Fischer-Tropsch process is as follows by equation (1) and (2):

$$CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2 \qquad (1)$$

$$CO + H_2 \rightarrow \text{Hydrocarbons} + \text{Oxygenated compounds} + H_2O \qquad (2)$$

FT synthesis have been realized recently (Bintulu in Malaysia, Oryx in Qatar) or are currently under construction (Pearl in Qatar, Escravos in Nigeria). The world consumption of crude oil in 2015 can be estimated as 20 million barrels per day. (Liang *et al.*, 2007).

FT synthesis was used in Germany during World War II to produce fuels from coal, and has been employed in SASOL, South Africa since the 1950s to produce fuels and chemicals. Shell has built a plant in Malaysia as a showcase of modern FT technology based on natural gas. Recently California air and energy officials in a California Air Resources Board (CARB) symposium praised the potential for gas-to-liquids (GTL), essentially FT synthesis, to make a significant future contribution to the state's diesel supply while reducing emissions and dependence on petroleum-based (shalchi, 2006).

1.1.2 Catalyst for Fisher-Tropsch

Cobalt and iron are the metals that were proposed by Fischer and Tropsch as the first catalysts for syngas conversion. Both cobalt and iron catalysts have been used in the industry for hydrocarbon synthesis. A brief comparison of cobalt and iron catalysts is given in Table 1.1.

Table 1.1: Comparison of Cobalt and Iron FT Catalysts (Khodakov *et al*., 2007)

Parameter	**Cobalt catalysts**	**Iron catalyst**
Cost	More expensive	Less expensive
Lifetime	Resistance to deactivation	Less resistance to deactivation
Activity at low conversion	Comparable	Comparable
Productivity at high conversion	Higher, less significant effect of water on the rate of carbon monoxide conversion	Lower, strong negative effect of water on the rate of carbon
Maximal chain growth probability	0.94	0.95
water gas shift reaction $CO + H_2O \rightarrow CO_2 + H_2$	Not very significant, more noticeable at high conversion	Significant
Maximal sulphur content	<0.1 ppm	<0.2 ppm
Flexibility (temperature and pressure)	Less flexible, significant influence of temperature and pressure on hydrocarbon selectivity	Flexible, methane selectivity is relatively low even at 613K

1.1.3 Application of Fisher-Tropsch Process and Product

In the twenty first-century, natural gas is expected to become an increasingly important raw material for manufacturing clean fuel and chemical. Fisher-Tropsch synthesis is the major part of gas to liquid technology, which is convert natural gas

into liquid fuel with very low sulphur and aromatic compound. Generally, the liquid fuels producing from GTL Technology consist of Synthetic LPG, Synthetic Naphtha, Synthetic Kerosine and Synthetic Diesel. Figure 1.2 shows the percentage of GTL products.

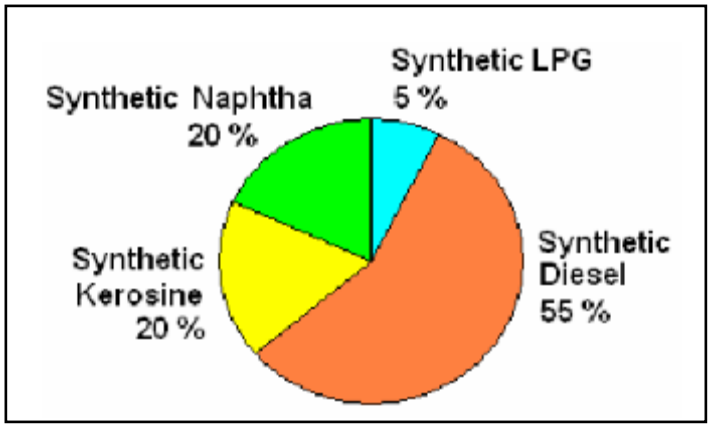

Figure 1.2: Percentages of the GTL products (Shalchi, 2006).

There is much factor that gives impact to the percentage of these product increases or decreases. The percentage of these products increase or decrease according to the kind of technology employed, nature of the catalyst, and the conditions of the reactions used. The properties of the GTL products are typical with regard of its combustion or its environmental affects. Since the light and mid synthetic products are the main and the most important products of the GTL industry. Therefore the significant care of the properties of these products play a great role in the promotion of the GTL industry (Shalchi, 2006).

The benefits of Fischer-Tropsch reactions is not restricted to producing valuable light and mid petroleum derivatives, but it also used to produce many valuable chemicals by only altering the operation conditions to change the growth of the hydrocarbon chains. Typical uses and applications are mentions on table 1.2 for other derivatives produced from fisher tropsch process that are valuable for daily life.

Table 1.2: Shows the typical uses and applications for different products produce after Fisher-Tropsch reaction (Shalchi, 2006):

Product Group	Typical uses and applications
Normal Paraffin's	Production of intermediates (LAB, SAS, alcohols). Production of intermediates for plasticizers, auxiliary chemical, manufacturing of film and special catalyst carrier and low polar odor-free all purposes solvents and diluents.
Mixed Paraffin's	Special low polar and odor-free solvent for paints, coating, dry cleaning, cleaners, insecticide and pesticide formulation, and drilling fluids.
Synthetic lubricants	Industrial and automotive lubricant applications including motor oils, compressor oil, hydraulic fluids, and grease.
Paraffin Wax	Manufacturing of candies, crayons, printing inks, potting and cables compounds, coatings, and packaging

1.2 Problem Statement

Catalyst is a vital part of any industrial FT process. FT process is a method for production of hydrocarbons from synthesis gas. The supported cobalt catalysts have been extensively used in FT process and have been found to be particularly convenient for the production of high hydrocarbons. In the future of industry, iron, cobalt and ruthenium are the best catalysts for FT synthesis polymers (Mukaddes, 2005).

But among them, cobalt catalysts are the preferred catalysts for FT synthesis based on natural gas because of their high activity for FT synthesis, high selectivity to linear hydrocarbons, low activity for the water gas shift (WGS) reaction, more stability toward deactivation by water (a by-product of the FT reaction),and low cost compared to Ru (Tavasoli *et al.*,2007).

The use of periodic mesoporous silica as supports for preparing Co-based FT synthesis catalysts has been recently explored by many researches because mesoporous have very high surface area characteristic that will allow high dispersions at higher cobalt loading as compared with conventional amorphous silicas (Martinez *et al*., 2003). In this research SBA-15 was used as a mesoporous silica support.

Numerous studies show that introduction of noble metals (Ru, Rh, and Pt) has strong impact on the structure and dispersion of cobalt species and FT reaction rates (Khodakov, 2009). But recently this noble's metal are higher in cost (Zhang *et al.*, 2003). As example Shell's plant in Malaysia employs cobalt catalysts. Ruthenium catalysts have excellent FT reactivity; however, no commercial ruthenium catalyst has ever been used, mainly due to its high cost. Ruthenium, zinc and has been used to improve the reduction and reactivity of cobalt catalysts (Zhang *et al.*, 2003). Thus, zinc was used as noble metal in this research because it's low price than other.

1.3 Objective

The objectives of this research are:

i. To synthesis SBA-15 as a support for catalyst.
ii. To synthesis Co-Zn/SBA-15 catalyst and study the effect of Co loading.
iii. To characterized Co-Zn/SBA-15 catalysts.

1.4 Scope of Study

To achieve the objectives, scopes have been identified in this research. Generally, the scopes of this research are focus on producing the new catalyst for FT synthesis which is Co-Zn/SBA-15 and the influence of cobalt and zinc promoter load

was investigated. Co-Zn/SBA-15 catalysts with same Zn defined with porous surface contents which 20 wt% and different Co contents which range 5 wt % until 15 wt % were prepared by incipient wetness impregnation of relative SBA-15 with desired amount of aqueous cobalt nitrate and zinc nitrate. The samples Co-Zn/SBA-15 catalyst was then characterized using Fourier Transform Infrared analysis (FTIR) and Scanning Electron Microscopy (SEM).

CHAPTER 2

LITERATURE REVIEW

2.1 Cobalt based catalyst

The FT synthesis process was shown to be catalyzed by certain transition metals, with Co, Fe, and Ru presenting the highest activity (Vannice, 1977). Among them, cobalt-based FT synthesis catalysts are usually preferred for the synthesis of long-chain paraffins (Iglesia *et al.*,1997) as they are more active per weight of metal, more efficient deactivation by water (a by-product of the FT synthesis reaction), less active for the competing water-gas shift (WGS) reaction, and produce less oxygenates than the iron-based systems. Ru-based catalysts are highly active but the high cost and low availability of Ru are important concerns limiting their commercial application (Schultz, 1999).

Significant efforts have focused on the optimization and tailoring of cobalt catalysts for specific applications. It has been demonstrated that cobalt active component, support, and promoter have important effects on the catalyst performance and structure (Schultz, 1999). Iglesia *et al.* (1997) reported that for relatively large cobalt particles (diameter > 10 nm), FT reaction rates were proportional to metal dispersion. Bartholomew (1984), Yermakov (1984), and De Jong (2006) observed that lower FT turnover frequencies with cobalt particles smaller than 6–8 nm. It seems that lower activity of small cobalt particles might be attributed to both their reoxidation at

the reaction conditions and modified electronic structure because of the quantum size effect.

A recent report by Loosdrecht (2007) reinforces that currently there is no consistent picture regarding oxidation of cobalt particles during FT reaction it was shown that reoxidation of cobalt metal particles in industrial FT reactors could be prevented by efficient control of water and hydrogen pressures. Thus, the observed decrease in FT productivity during the reaction likely cannot be assigned solely to cobalt particle oxidation. Analysis of the literature suggests that a highly active cobalt catalyst would require optimal-sized of cobalt metal particles, high reducibility, and high stability of cobalt active sites.

2.2 SBA-15 Supported cobalt based catalyst

SBA-15 is one member of a family of mesoporous silicas that make ideal candidates for catalyst supports by covalent grafting (Wight *et al.*, 2002). It is an ordered, amorphous silica material first created by Zhao and Stucky in 1998, in an effort to increase the material's thermal stability via increased wall thickness relative to MCM type materials .The improved hydrothermal and thermal stability makes them the most promising catalytic materials (Zhao *et al.*, 1998). These materials have important applications in a wide variety of fields such as separation, catalysis, adsorption and advanced nanomaterials.

Mesoporous materials (SBA-15) are porous materials with pore diameters in the range of 2-50 manometers (Xia *et al.*, 2003). SBA-15 is by far the largest pore size mesoporous material with highly ordered hexagonally arranged mesochannels, with thick walls, adjustable pore size from 3 to 30 nm, and high hydrothermal and thermal stability.SBA-15, which possesses larger pores, thicker walls and higher thermal

stability as compared other mesoporous silicas may be used a promising catalyst support, particularly for reactions occurring at high temperatures (Wang *et al.*, 2004).

Figure 2.1 shows the preparation of SBA-15 materials in a template process in acidic conditions with poly (alkaline oxide) tri-block co-polymers (Mukaddes, 2005). In acidic, aqueous solution, a structure directing agent (triblock copolymer of poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide)) is dissolved to form micelles. These block copolymers self-assemble to form unidirectional, cylindrical micelles in hexagonal arrays. Tetraethylorthosilicate (TEOS) is added to the solution, which polymerizes around the organic micelles forming the pore walls of the material. Finally, after filtration and washing, the material is calcined to combust the organic structure directing agent, leaving the mesoporous SBA-15 silica (Zhao *et al., 1998*).

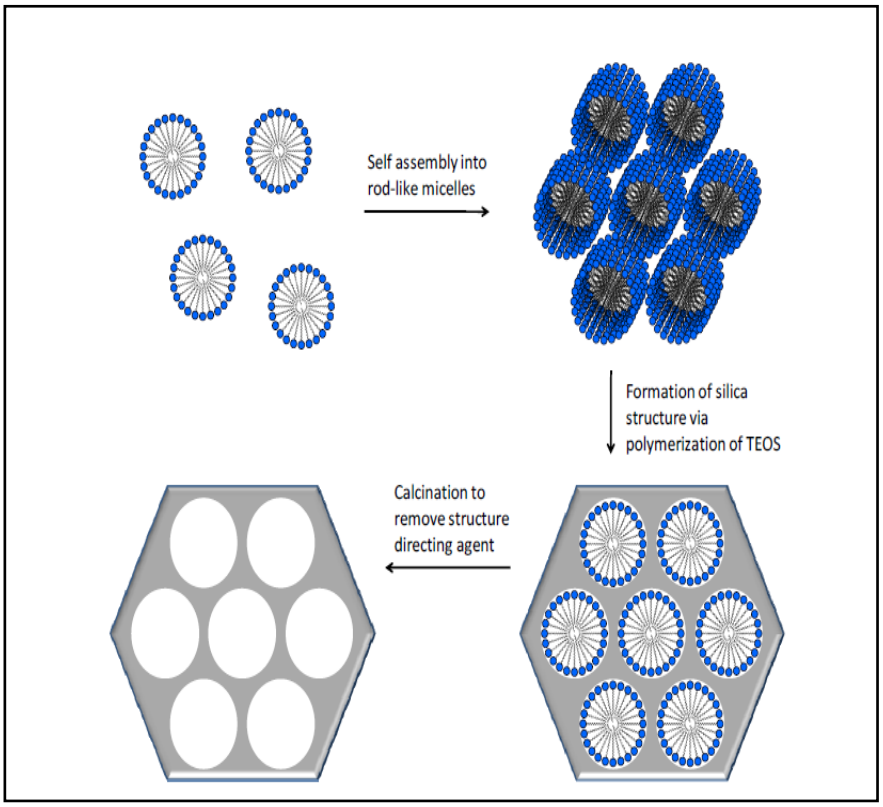

Figure 2.1: Synthesis of SBA-15 mesoporous silica (Mukaddes, 2005)

TEM result at Figure 2.2 showed the SBA-15 ordered structure of the material, and shows the cylindrical pores are arranged in an ordered hexagonal array (Akca, 2006). Recently, there are various studies carried out using SBA-15 as support. For example, SBA-15 supported $FePO_4$ show higher CH_4 conversion and HCHO selectivity than unsupported SBA-15 and MCM-41 supported one. The larger porous diameter and the `inertness' of SBA-15 were probably responsible for the higher HCHO selectivity of the SBA-15 supported catalysts as compared with the MCM-41 supported ones particularly with low loading amount of $FePO_4$ (Wang *et al.*, 2004).

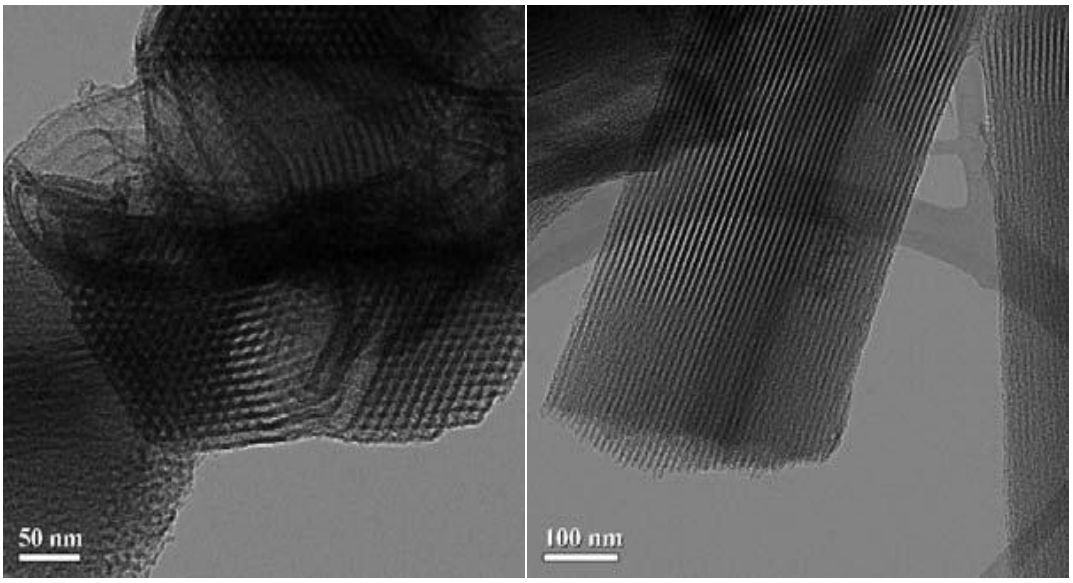

Figure 2.2: TEM images of pure SBA-15(Akca, 2006)

In another study, by using SBA-15 supported iron (II)-bisimine pyridine catalyst was synthesized for ethylene polymerization. In polymerization, they found the supported catalyst can successfully control the morphology of polyethylene and the supported catalyst has fairly high catalytic activity for ethylene polymerization. (Akca, 2006).

As another example, impregnation of Co into MCM-41 and SBA-15 were implemented. It is observed that catalysts supported by SBA-15 are 5-10 times more active than supported by MCM-41. While MCM-41 structure collapsed after impregnation and BET surface area decreased with adding much amount of Co impregnation, SBA-15 structure leaded to no destruction of ordered structure (Mukaddes, 2005).

By adding noble metals or metal oxides, physical and chemical properties of mesoporous materials are improved (Mukaddes, 2005). However, it is very difficult to introduce the metal ions into SBA-15 directly due to the difficulties in the formation of metal –O–Si bonds under the strong acidic conditions for the synthesis of SBA-15 materials. Under strong acidic conditions, the metal ions will exist in the cationic form other than their corresponding oxo species (Mukaddes, 2005).

Notably, many efforts have been devoted to the incorporation of Al, Ti and V into SBA-15, including the two-steps pH adjusting methods (Li *et al.,* 2004), the hydrolysis-controlled methods (Li *et al.,* 2004 and Zhang *et al.,* 2002) and microwave hydrothermal procedures (Chen *et al.,* 2004).

Mesoporous materials also have attracted significant attention in related fields of academia and industry, and have been widely applied as catalysts in petrochemical industry. However, the low acidity and hydrothermal stability limited their application in environmental catalysis, such as selective catalytic reduction (SCR) of NO in the presence of oxygen (Liang *et al.,* 2007). SBA-15 has adjustable pore diameter, thick pore wall and excellent hydrothermal stability. Therefore, it is probably appropriate to be used in SCR of NO with ammonia (Liang *et al.,* 2007).

2.3 Effect of Cobalt Loading

One important focus in the development of these catalysts is the improvement of the catalyst activity by increasing the number of active metal sites that are stable under reaction conditions. However, due to the strong interactions of cobalt species with the support more insight is needed into understanding the effect of the loading and size distribution on both the physico-chemical properties and performance of these catalysts (Tavasoli *et al.,* 2005). Surprisingly, there have limited studies have been reported in which systematically explored.

Iglesia *et al*. (1997) showed that the FT synthesis rates per total cobalt atoms increase linearly with increasing metal dispersion irrespective of the nature of the support used. In other words, the turnover rates are not influenced by support identity, and thus the catalyst activity should be proportional to the number of surface cobalt metal (Co) sites.

Jacobes *et al*. (2002) have shown that, increasing the cobalt loading, will improve the reducibility by decreasing the interactions with the support. By working at atmospheric pressure and differential conditions, Khodakov *et al*. (2007) observed an increase of the turnover rates by increasing the particle size of cobalt supported on mesoporous silicas of different pore size.

More recently Tavasoli *et al*. (2005) had done a research in addition of different loadings of Re and Ru to 15 wt % Co/Al_2O_3 catalyst. The result has shown the final density of active Co sites depends on two main parameters, i.e., cobalt dispersion and the degree of reducibility of the supported oxidize cobalt species. Ideally, optimum cobalt catalysts should be prepared by achieving high dispersions of highly reducible cobalt species at cobalt loadings as high as possible. But due to high cost of cobalt, it is important to determine the appropriate loading of cobalt to maximize the availability of active cobalt surface sites for participation in the reaction, after catalyst activation.

2.4 Effect of Zinc Promoter

The goal of promotion is to enhance cobalt FT catalysts by the addition of small amount of noble metals and metal oxide. Numerous studies have shown that introduction of noble metals such as (Ru, Co, Zn, Pt, and Pd) has strong impact on the structure and dispersion of cobalt species. As example, analysis of the literature data suggest that introduction of noble metals could result on following phenomena (Khodakov, 2009):

- Ease cobalt reduction
- Enhancement of cobalt dispersion
- Better resistance to deactivation.
- Modification of intrinsic activity of surface site.

In order to gain access active site, noble metal promoters are often employed. These noble metal promoters, such as Pt or Ru, reduce at a lower temperature than the cobalt oxides, and catalyze cobalt reduction, presumably by hydrogen spill over from the promoter surface area (Wei *et al.,* 2001). However, the promotion with small amount of noble metal does not usually have noticeable effect on mechanical properties of cobalt supported catalysts (Wei *et al.*, 2001). Thus, addition of small amounts of noble metal only shifts the reduction temperature of cobalt oxides and cobalt species interacting with the support to lower temperatures (Wei *et al.,* 2001).

Due to the added expense of the promoter, it is important to determine the appropriate loading of promoter to maximize the availability of active cobalt surface sites for participation in the reaction, after catalyst activation.

Textural promoters, such as catalyst supports and support modifiers, are used typically to increase the dispersion of the clusters, improve attrition resistance, enhance sulphur tolerance, or electronically modify the active metal site (Hilmen *et al.*, 1996).

Numerous studies have shown that by using nobles metals such Ru, Pt, and Pd are more explore by many researcher ,but by using zinc as promoter is a new development of promoter because the price are lower than other (Tavasoli *et al*.,2007).

2.4.1 Cobalt Dispersion

The presence of noble metal can affect particle size of both cobalt oxide and metallic cobalt. Analysis data suggests that the promotion with noble metals primarily reduces the sizes of cobalt oxide particles in weakly interacting supports, *e.g*. silica. The increase in cobalt dispersion in the presence of platinum in silica supported catalysts was observed by Schanke *et al*. (1995). In that work, the extent of reduction in the monometallic and Pt-promoted cobalt catalysts was close to 90%. The improvement in catalytic activity on promotion with Pt was attributed to the enhancement in cobalt dispersion. Higher cobalt dispersion was also observed by Tsubaki *et al*. (2001) in Pt and Pd promoted cobalt silica supported catalysts. Mauldin *et al*. (2001) reported that rhenium promotion increased cobalt oxide dispersion during preparation of Co/TiO_2 supported catalysts.

Promotion with noble metals can also affect the sizes of cobalt metal particles in the reduced cobalt catalysts. Increase in the surface area of metallic cobalt was observed after promotion of 20% Co/Al_2O_3 catalysts with Pt, Ir, Re, or Ru (Shahnon *et al*., 2007). The effect of promotion with platinum on cobalt dispersion in the reduced catalysts was rather significant with cobalt alumina supported catalysts (Chu *et al*., 2007).

In contrast to silica supported counterparts, in alumina supported catalysts, promotion with Pt did not result in a decrease in the sizes of cobalt oxide particles in the calcined catalysts. At the same time, the average size of cobalt metallic particles was smaller in the catalysts promoted with Pt than in the monometallic counterparts.